

Supporting Information

BN-Decorated Graphene Nanoflakes for Tunable Opto-electronic and Charge Transport Properties

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Computational Details:

All the quantum chemical calculations in this work are performed using density functional theory (DFT), as implemented in Gaussian-09¹ software package. We have used Becke three parameters exchange with Lee-Yang-Parr correlation (B3LYP)² hybrid functional for all calculations involving the monomers and the dispersion corrected non-local functional, ωB97XD, is employed for the geometry optimizations of the dimers for accounting of the dispersion interactions. The latter functional has been shown to correctly determining the stacked geometry and associated energy. B3LYP is chosen as the suitable functional for electronic structure calculations as was demonstrated in many previous studies dealing with PAHs.³ All geometry optimizations are carried out using the basis set 6-31+g(d,p), at the ground state, with neutral charge and singlet electronic state configuration. The geometries are confirmed to be at local minimum energy structures by analysing the vibrational frequencies.

To understand the aromatic nature, we calculate Nucleus Independent Chemical Shifts (NICS) to assess the magnetically-defined aromatic character of coronene and its imide derivatives as well as of the full-BN substituted and partial BN substituted systems, by the Gauge-Invariant Atomic Orbital (GIAO) method at B3LYP/6-31+g(d,p) level of theory.⁴ NICS, as proposed by Schleyer *et. al.*, is the negative of the absolute shielding, computed at the ring centre NICS(0) and NICS(1) is calculated 1 Å above or below the ring centre.⁵ The reorganization energy (λ) is calculated employing the following formulae:

$$\lambda_{electron} = (E_-^* - E_-) + (E_{anion}^* - E)$$

$$\lambda_{hole} = (E_+^* - E_+) + (E_{cation}^* - E)$$

where E represents the ground state energy of the optimized geometry of the neutral molecule, E_- (E_+) is the energy of the optimized anionic (cationic) species, E_-^* (E_+^*) is the energy of the anionic (cationic) molecule in neutral geometry, and E_{anion}^* (E_{cation}^*) is the energy of the neutral molecule in anionic (cationic) geometry. Time dependent density functional theory (TDDFT), as implemented in Gaussian 09, have performed using B3LYP/6-31+g(d,p) level of theory in gas phase for the excited state properties. We also performed periodic calculations for investigating bulk electronic properties using the dispersion-corrected GGA/PBE+D (dispersion) density functional employing an extended plane wave basis code, VASP⁶, implementing the projected augmented wave PAW⁷ method. The exchange and correlation functional invoked here takes into account the van der Waals interactions which are important for the crystal systems studied here.

In addition, we have estimated the charge (hole and electron) transfer integrals for gaining deeper understanding of their charge transport properties. In general, for organic semiconductors, the hopping process is modelled through a non-adiabatic electron-transfer process within the semi-classical Marcus-Hush formalism.⁸ The charge transfer integrals or hopping matrix elements, site energies and spatial orbital overlap are calculated by fragment orbital method, using the Amsterdam Density Functional (ADF) program.⁹ For all ADF calculations, we have used Generalized Gradient Approximation (GGA) within Perdew-Burke-Ernzerhof (PBE)¹⁰ as exchange and correlation functional, and a large triple zeta (ζ) with double polarization (TZ2P) basis set for all atoms. We have taken into account the dispersion interactions for calculating the charge transfer integrals of π -stacked systems. The effective charge transfer integral (J_{eff}) calculated using the formula:

$$J_{\text{eff}} = J_{ij} - \left(\frac{1}{2}\right) S_{ij} (\varepsilon_i + \varepsilon_j)$$

where, J_{ij} and S_{ij} denote the transfer integral and spatial overlap matrix element between i^{th} and j^{th} molecular fragment orbitals (HOMO for hole transfer and LUMO for electron transfer); ε_i and ε_j represent the site energies of the two molecular orbitals where charges are localized. In this approach, the dimer molecular levels are represented as the linear combination of individual monomer molecular orbitals and the charge transfer integral is obtained as the off-diagonal elements of the Kohn-Sham Hamiltonian, $H_{\text{KS}} = \text{SCEC}^{-1}$.

The hopping rate of a charge carrier can be defined by Marcus theory formalism¹¹ given as:

$$W = \frac{2J_{eff}^2}{h} \sqrt{\frac{\pi^3}{\lambda k_B T}} \exp\left(\frac{-\lambda}{4k_B T}\right)$$

where k_B is Boltzmann constant and T is the temperature in absolute scale (here $T=300$ K).

The diffusion coefficient (D) which is related to the hopping rate is given by,

$$D = \frac{1}{2d} \frac{\sum_i r_i^2 W_i^2}{\sum_i W_i}$$

here, d =dimensionality of the crystal ($d=3$ for all crystals considered here), and r is the centre of mass distances of the adjacent molecules from a central molecule. D is normalized over the total probability of charge transfer. Then, the final drift mobility (μ) is calculated using the Einstein relation, as follows:

$$\mu = \frac{e}{k_B T} D$$

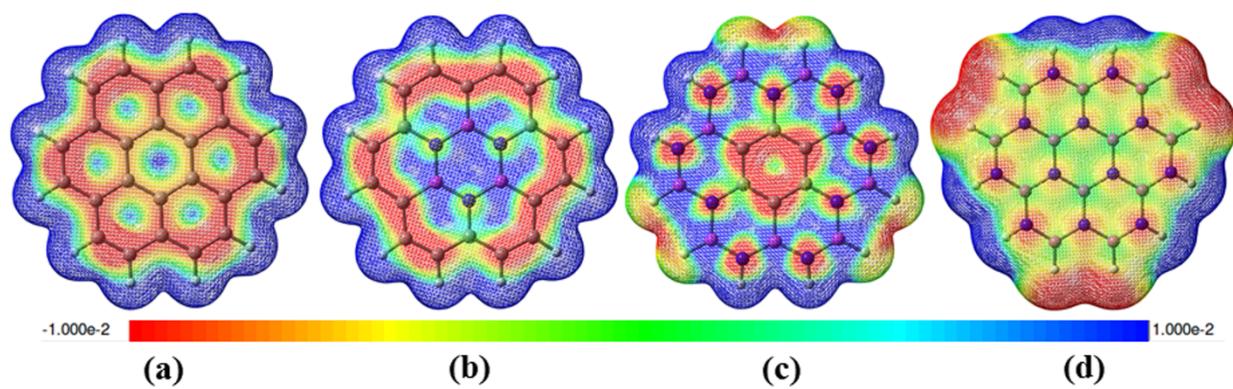


Figure S1. Iso-surfaces of computed electrostatic potential (ESP) of (a) coronene, (b) mid-BN-coronene, (c) peri-BN-coronene, and (d) full-BN-coronene.

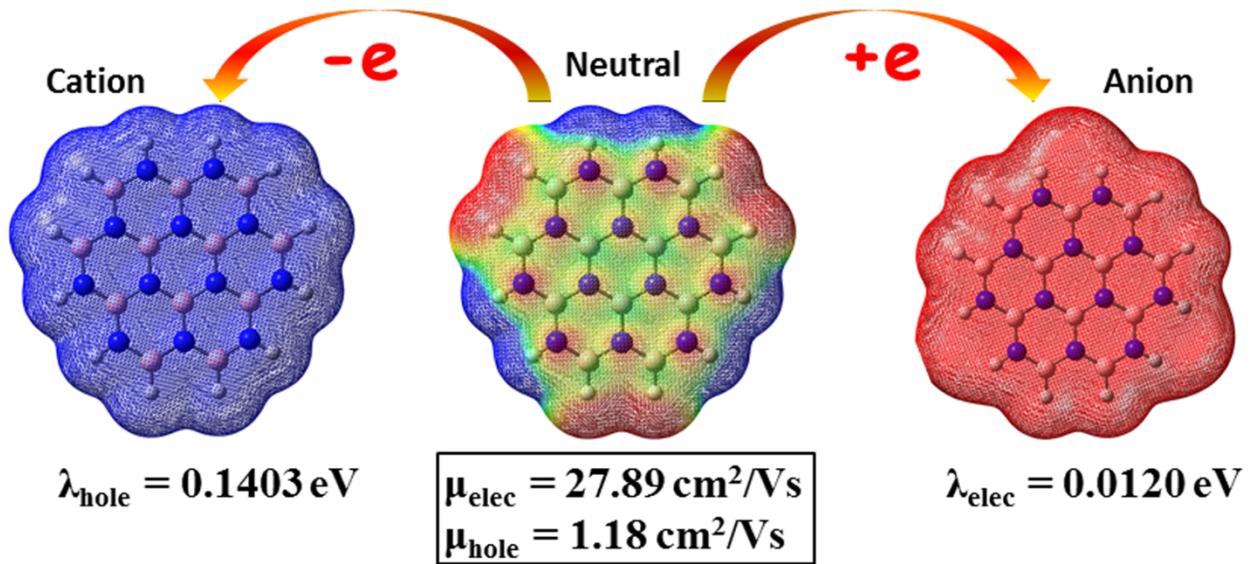


Figure S2: ESP Plot of cation (left), neutral (middle) and anion (right) of full-BN-coronene.

Table S1: Reorganization energy values calculated using B3LYP/6-31+g(d,p) for all four systems and the values calculated using M062X/6-31+g(d,p) and LSDA/6-31+g(d,p) level for full-BN-coronene are listed.

| System | λ_{hole} (eV) | $\lambda_{\text{electron}}$ (eV) |
|--------------------------|------------------------------|----------------------------------|
| coronene | 0.1266 | 0.1673 |
| mid-BN-coronene | 0.1244 | 0.1591 |
| peri-BN-coronene | 0.3564 | 0.2392 |
| full-BN-coronene (B3LYP) | 0.1403 | 0.0120 |
| full-BN-coronene (M062X) | 0.2544 | 0.0267 |
| full-BN-coronene (LSDA) | 0.4708 | 0.0204 |

Table S2: Effective charge transfer integral (J_{eff}) for various neighbors present in cluster model.

| System | R_{ij} (Å) | $J_{\text{eff}}^{\text{hole}}$ (eV) | $J_{\text{eff}}^{\text{elec}}$ (eV) |
|----------|--------------|-------------------------------------|-------------------------------------|
| coronene | 4.47 | -0.151 | -0.101 |
| | 8.01 | 0.002 | 0.002 |

| | | | |
|-------------------------|-------|--------|--------|
| | 9.73 | 0.005 | -0.020 |
| | 10.70 | 0.002 | 0.008 |
| mid-BN-Coronene | 4.52 | -0.126 | -0.056 |
| | 7.63 | 0.004 | -0.001 |
| | 9.74 | 0.004 | 0.022 |
| | 10.74 | 0.001 | 0.010 |
| peri-BN-coronene | 4.48 | -0.130 | 0.067 |
| | 7.54 | 0.008 | -0.004 |
| | 9.70 | 0.005 | -0.005 |
| | 10.68 | -0.002 | 0.012 |
| full-BN-coronene | 4.35 | -0.093 | -0.131 |
| | 7.78 | 0.019 | 0.017 |
| | 9.77 | -0.005 | 0.012 |
| | 10.69 | -0.002 | 0.001 |

[j = 2, 3, 4, 5]

Table S3. Electronic excitation energies with oscillator strengths and relevant MOs contribution for each excitation obtained for the larger sizes h-GNF with varying BN substitutions calculated using TDDFT. The electronic HOMO-LUMO orbital gaps (ΔE_{H-L}) are also provided. The systems refer to the structures shown in Fig. 6.

| System | Transition Energy (eV) | Oscillator Strength (f) | MO contributions (weight) | Wavelength (nm) | ΔE_{H-L} (eV) |
|------------|------------------------|-------------------------|---------------------------|-----------------|-----------------------|
| (a) | 2.16 | 1.17 | H > L (0.35) | 573.81 | 2.10 |
| | 2.16 | 1.17 | H-1 > L (0.35) | | |
| (b) | 1.99 | 1.27 | H > L+1 (0.39) | 620.50 | 1.87 |
| | | | H-1 > L (0.39) | | |
| | 1.99 | 1.27 | H-1 > L+1 (0.40) | | |
| | | | H > L (0.39) | | |

| | | | | | |
|------------|------|-------|-------------------|--------|------|
| (c) | 2.24 | 0.58 | H → L+1 (0.38) | 554.69 | 2.44 |
| | | | H-1 → L (0.38) | | |
| | 2.24 | 0.58 | H-1-> L+1 (0.38) | | |
| | | | H -> L (0.38) | | |
| (d) | 1.88 | 1.51 | H → L (0.49) | 658.79 | 1.75 |
| | 1.88 | 1.51 | H → L+1 (0.49) | | |
| (e) | 5.91 | 0.35 | H-1 -> L+3 (0.29) | 209.71 | 6.07 |
| | 5.91 | 0.35 | H -> L+3 (0.30) | | |
| (f) | 4.73 | 0.831 | H -> L+2 (0.39) | 262.32 | 5.02 |
| | | | H-1 -> L (0.39) | | |
| | 4.73 | 0.832 | H-1 -> L+1 (0.39) | | |
| | | | H -> L (0.39) | | |
| (g) | 3.32 | 1.023 | H -> L+1 (0.47) | 373.48 | 3.46 |
| | | | H-1 -> L+1 (0.47) | | |
| | 3.32 | 1.022 | H-1 -> L+1 (0.47) | | |
| | | | H -> L (0.47) | | |
| (h) | 2.54 | 1.16 | H -> L+1 (0.44) | 488.44 | 2.58 |
| | 2.54 | 1.16 | H-1 -> L+1 (0.44) | | |

References:

1. Frisch, M. J.; Trucks, G. W.; H. B. Schlegel; G. E. Scuseria; M. A. Robb, J. R. C., G. Scalmani, V. Barone, B. Mennucci,; G. A. Petersson, H. N., M. Caricato, X. Li, H. P. Hratchian,; A. F. Izmaylov, J. B., G. Zheng, J. L. Sonnenberg, M. Hada,; M. Ehara, K. T., R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima,; Y. Honda, O. K., H. Nakai, T. Vreven, J. A. Montgomery, Jr.,; J. E. Peralta, F. O., M. Bearpark, J. J. Heyd, E. Brothers,; K. N. Kudin, V. N. S., R. Kobayashi, J. Normand,; K. Raghavachari, A. R., J. C. Burant, S. S. Iyengar, J. Tomasi,; M. Cossi, N. R., J. M. Millam, M. Klene, J. E. Knox, J. B. Cross,; V. Bakken, C. A., J. Jaramillo, R. Gomperts, R. E. Stratmann,; O. Yazyev, A. J. A., R. Cammi, C. Pomelli, J. W. Ochterski,; R. L. Martin, K. M., V. G. Zakrzewski, G. A. Voth,; P. Salvador, J. J. D., S. Dapprich, A. D. Daniels,; O. Farkas, J. B. F., J. V. Ortiz, J. Cioslowski,; and D. J. Fox, G., Inc., Wallingford CT. 2009.
2. (a) Becke, A. D., *Phys. Rev. A* **1988**, 38 (6), 3098-3100; (b) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J., *J. Phys. Chem.* **1994**, 98 (45), 11623-11627.
3. (a) Randić, M., *Chem. Rev.* **2003**, 103 (9), 3449-3606; (b) Feng, X.; Li, Q.; Gu, J.; Cotton, F. A.; Xie, Y.; Schaefer, H. F., *J. Phys. Chem. A* **2009**, 113 (5), 887-894; (c) Del Bene, J. E.; Yáñez, M.; Alkorta, I.; Elguero, J., *J. Chem. Theory Comput.* **2009**, 5 (9), 2239-2247.
4. (a) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v. E., *J. Am. Chem. Soc.* **1996**, 118 (26), 6317-6318; (b) Ditchfield, R., *Mol. Phys.* **1974**, 27 (4), 789-807; (c) Wolinski, K.; Hinton, J. F.; Pulay, P., *J. Am. Chem. Soc.* **1990**, 112 (23), 8251-8260.
5. von Ragué Schleyer, P.; Manoharan, M.; Wang, Z.-X.; Kiran, B.; Jiao, H.; Puchta, R.; van Eikema Hommes, N. J. R., *Org. Lett.* **2001**, 3 (16), 2465-2468.
6. (a) Kresse, G.; Furthmüller, J., *Phys. Rev. B* **1996**, 54 (16), 11169-11186; (b) Kresse, G.; Furthmüller, J., *Comput. Mater. Sci.* **1996**, 6 (1), 15-50.
7. (a) Blöchl, P. E., *Phys. Rev. B* **1994**, 50 (24), 17953-17979; (b) Kresse, G.; Joubert, D., *Phys. Rev. B* **1999**, 59 (3), 1758-1775.
8. (a) Bromley, S. T.; Mas-Torrent, M.; Hadley, P.; Rovira, C., *J. Am. Chem. Soc.* **2004**, 126 (21), 6544-6545; (b) Marcus, R. A., *Rev. Mod. Phys.* **1993**, 65 (3), 599-610; (c) Berlin, Y. A.;

Hutchison, G. R.; Rempala, P.; Ratner, M. A.; Michl, J., *J. Phys. Chem. A* **2003**, *107* (19), 3970-3980.

9. te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Fonseca Guerra, C.; van Gisbergen, S. J. A.; Snijders, J. G.; Ziegler, T., *J Comput Chem* **2001**, *22* (9), 931-967.
10. Burke, K.; Perdew, J. P.; Ernzerhof, M., *Int. J. Quantum Chem* **1997**, *61* (2), 287-293.
11. (a) Marcus, R. A., *J. Chem. Phys.* **1956**, *24* (5), 966-978; (b) Marcus, R. A., *J. Chem. Phys.* **1956**, *24* (5), 979-989; (c) Marcus, R. A., *J. Chem. Phys.* **1957**, *26* (4), 872-877; (d) Marcus, R. A., *Discuss. Faraday Soc.* **1960**, *29* (0), 21-31; (e) Marcus, R. A., *J. Chem. Phys.* **1965**, *43* (2), 679-701; (f) Marcus, R. A.; Sutin, N., *Biochimica et Biophysica Acta (BBA) - Reviews on Bioenergetics* **1985**, *811* (3), 265-322.